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## IDENTIFICATION OF CONTAMINATION SOURCES IN ESTUARINE WATER BY MULTIWAY DATA ANALYSIS. A CASE OF STUDY: ESTUARY OF THE NERBIOI-IBAIZABAL RIVER

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### Abstract

Chemometric data analysis methods have been proposed to extract useful information from monitoring studies. The environmental data sets are frequently multidimensional and have a complex structure with thousand of numbers usually highly correlated each other.

In this work, it is suggested to compare two-way (Principal Component Analysis (PCA)) with three-way (Parallel Factor Analysis (PARAFAC) and Tucker3) multivariate methods, to identify possible changes and sources in trace element concentration over the monitoring period for estuarine waters.

The study was focused in the metal concentration of the estuary of the Nerbioi-Ibaizabal River. This estuary is an area that has been subjected an extreme industrial and mining activity throughout its history, and it is located in one of the most important urban areas (Bilbao, Basque Country) of the Cantabrian sea coast. Correct environmental policies started to be implemented in the 90's and they have led to a remarkable recovery of the ecosystem. But their sediments from its bed, however, still show an important metallic content.

In an effort to study the evolution and identify spatial and seasonal trends in metallic pollution, superficial (top 10 cm) and deep (in contact with the sediment) water samples were collected at eight different points (four in tributary rivers, one in a closed dock, two in the main channel and another one in the mouth of the estuary) at the estuary of the Nerbioi-Ibaizabal River, both at low and high tides, approximately every three months from January 2005 to December 2010 (19 sampling campaigns). After filtering and acidifying the samples, they were analysed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) to simultaneously determine the concentration of Al, As, Cr, Cu, Fe, Mn, Ni and Zn.

The results of the three models applied (PCA, PARAFAC and Tucker 3) led to similar conclusions about geographical variations, giving information of the current situation of the estuary. In addition, differences between the trace elements were observed. The first group was formed by Cu, As and Fe and the second one by Al, Cr, Mn, Ni and Zn.

Application of the three-way methods (PARAFAC and Tucker3) provided us with some extra information about the temporal evolutions of the metal concentrations was found. Most of the spring samplings presented high concentration values for As, Cu and Fe and low concentration of Al, Cr, Mn and Zn.

**Keywords** - Estuarine waters, trace elements, monitoring programs, chemometric analysis, Principal Component Analysis, Tucker3, Parallel Factor Analysis



## INTRODUCTION

The E.U. Water Framework Directive (2000/60/EC) was introduced in October 2000 in order to restore the quality of surface and ground waters, and to achieve chemical, ecological and quantitative good status in the aquatic environment by 2015 [1].

Estuarine and coastal zones are the sites of major discharges of urban and industrial pollutants which accentuate pollution problem. Considerable amounts of metals originated from polluting activities or physical processes, enter the marine environment through rivers and affect the estuarine systems [2].

In this context, chemometric data analysis methods have been introduced for the identification of sources of metallic substances (natural or anthropologic) and risks in the aquatic environment. These methods allow the transformation of complex data set, for example, monitoring of water samplers collected at different sites during a long period of years, in different components to extract information and to a better understanding of the data collected.

Traditionally, bidimensional models like Principal Component Analysis (PCA) or Multivariate Curve Resolution using Alternating Least Squares (MCR-ALS) [3, 4] have been used to environmental analysis with good results. But recently, PARAFAC [5, 6] and Tucker 3 [7] like three-way models have been shown to be effective tools for interpreting extensive environmental dataset.

In our case, the estuary of the Nerbioi-Ibaizabal River is located in the south-east corner of the Bay of Biscay and is one of the most populated areas on the Cantabrian coast (about one million people). A great deal of metallurgical activity started in the surroundings at the end of the XIX century, due to the wealth of mineral resources in the region, especially iron. The next 100 years were characterised by a constant degradation of the estuary, with an uncontrolled release of organic and inorganic pollutants into the system [8]. The decline of industrial activity, closure of mines and implementation of environmental protection policies have resulted in a progressive recovery of the estuary since the early 1980s [9]. Nevertheless, the estuary still presents considerable pollution levels, both in water and sediments [10-15].

The aim of this work was to obtain an extended database on the distribution of trace elements concentration along the estuary and to know if chemometric three-ways models could be good tools for the identification of contamination sources.

## EXPERIMENTAL

### *Sampling area*

Superficial (top 10 cm) and deep (in contact with the sediment) water samples were collected from 2005 to 2009 at eight different points of the estuary, both at low and high tides.

Water was collected at each point with a 2 L Van Dorm type all-plastic water sampler (KD Denmark, Research Equipment, Silkeborg, Denmark), specifically designed for trace metal sampling. The sampler was dropped into water and carefully allowed to go down until it came into contact with the sediment. Then, it was raised to about 5 cm above the river bed and kept in this position for 3 min. Afterwards the messenger was dropped to close the system and the sampler was recovered. The sampler was drained and the sampling procedure was repeated. The second water sample was used first to homogenise 500 mL HNO<sub>3</sub> pre-cleaned crystal bottle and then to fill it to the top. The bottle was protected against light using aluminium foil and transported to the lab in a cool box. Blank samples (pre-cleaned bottles filled with Milli-Q quality water at the beginning of the sampling day) were handled in a similar way.

In the laboratory, the water samples were filtered through 0.45 µm cellulose filters (Whatman) in a precleaned standard borosilicate vacuum system and acidified with 5 mL of 69% HNO<sub>3</sub>. The acidified samples were stored in 50 mL polyethylene vials at 4 °C and protected against light until analysis. The concentrations of Al, As, Cr, Cu, Fe, Mn, Ni, and Zn were simultaneously measured by ICP/MS (Elan 9000, Perkin Elmer, Boston, MA), using the external calibration method with internal standard correction.



### Data pre-treatment

For the application of the two-way methods (PCA and MCR-ALS) the bidimensional data augmentation was obtained placing the different sampling campaigns one on top of the other, so the dimensions of the augmented data matrix were 544 x 8 (8 sites x 2 low and high tide x 2 superficial and proof deep x 17 campaigns and 8 variables).

For the creation of the three-way augmented data, the 19 sampling campaigns were placed one behind the other. In this occasion 3 loading matrices were created after the data set augmentation: loadings of the first mode (also called scores for two-way data) contained the sampling sites, deep and tide, the loadings of the second mode, contained the metal composition (loadings for two-way data) and the loadings in third mode contained the different sampling campaigns.

Values below the detection limit (LOD) were replaced for their half (LOD/2), which was shown to give better results than substitution by LOD or zero [16].

Data pre-treatment and analysis of data sets were performed under the MATLAB v.7.0 (The Mathworks, MA, USA) using the PLS-Toolbox v.3.5 (Eigenvector Research Ltd., WA 98801 Manson, MA, USA).

## RESULTS

After the application of the two-way methods (PCA and MCR-ALS) differences between the trace elements were observed. The first group was formed by Cu, As and Fe and the second one by Al, Cr, Mn, Ni and Zn (Fig.1.a). Scores of PCA with the different sampling sites can be seen in the Figure 1.b.

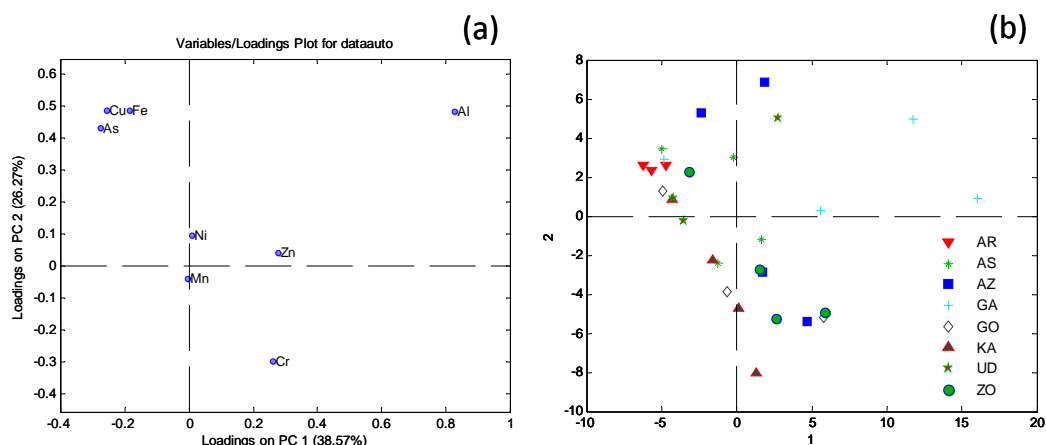


Figure 1. a) Loadings plot of PCA for the first and the second principal components, b) Scores of PCA for the first and the second principal components (AR, AS, AZ, GA, GO, KA, UD and ZO are different sample points).

By the application of the three-way methods, for comparing with the results obtained with the bidimensional methods, some extra information about the temporal behaviour was found. Most of the spring samplings presented high concentration values for As, Cu and Fe and low concentration of Al, Cr, Mn and Zn (Fig.2).

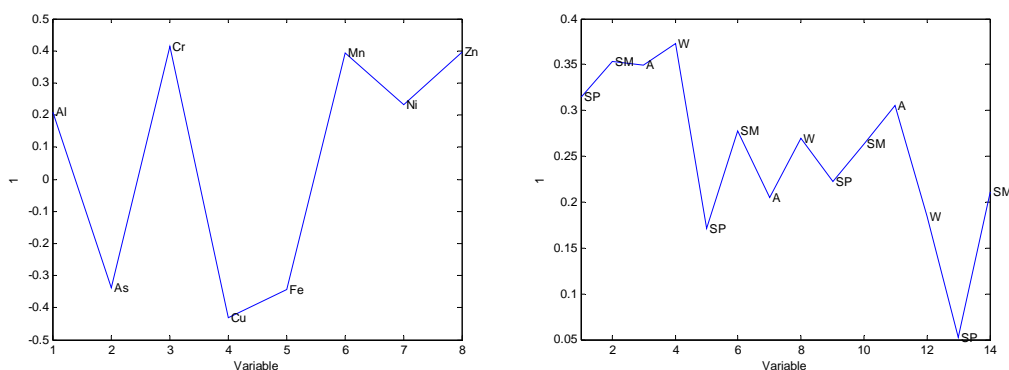


Figure 2. Plot of the loadings of the second mode explained by the first and the second components for the PARAFAC model (SP: spring, SM: summer, A: autumn and W: winter).

## CONCLUSION

The chemometric data analysis method, including two-way and three-way methods, was found to be a useful tool for the identification of contamination patterns and sources of metals in the estuary of Nerbioi-Ibaizabal from 2005 to 2009.

In this work, the three models applied (PCA, PARAFAC and Tucker3) led to similar conclusions about geographical variations, giving information of the current situation of the estuary. By all models obtained, the loadings were divided in two groups. Always As, Cu and Fe appeared together and the other trace elements formed the second group.

Nonetheless three-way (PARAFAC and Tucker3) models provided more information about of temporal evolution of the metal concentrations.

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